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# Conversion of methanol to aromatics in fluidized bed reactor

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ABSTRACT

Conversion of methanol to aromatics (MTA) was conducted over a fresh or a spent Zn/ZSM-5 catalyst in single stage fluidized bed (SSFB) and two stage fluidized bed (TSFB). Sampling at different stages of TSFB and operation in the temperature range of 250, 275, 300, 325, 350, 380 and 475 °C revealed the consecutive reaction mode from methanol to DME, $C_1$–$C_4$ hydrocarbons, $C_{5+}$ nonaromatics to aromatics finally. High weight ratio of *para*-xylene (PX) in xylene in wide temperature range suggested that PX was the primary product of MTA, and other xylenes are produced by the iosmerization of PX. Other aromatics such as benzene, toluene and trimethylbenzene are finally produced by the dealkylation, alkylation or disproportionation of xylene. The adoption of TSFB reactor was effective to increase the yield of aromatics, compared to that using SSFB, due to the inhibition of backmixing of gases. Combination of TSFB and highly active catalyst with strong acids was effective to get high yield of aromatics under high space velocity of methanol.

## 1. Introduction

Although aromatics, very important basic chemicals, were dominantly produced from oil-based route to this date, the gradual depletion of oil reserve resulted in the sustainably tight supply and high cost of aromatics. In the past two decades, the route of converting methanol into aromatics (MTA) received intensive attention considering methanol was easily available from wide resources such coal, natural gas, shale gas and biomasses [1,2]. Technically, the single pass conversion of methanol, over Zn or Cu or Ga supported on ZSM-5 catalyst at 470–500 °C, gave the aromatics yield of 50–70% (carbon base), the yield (25–40%) of gaseous hydrocarbon ($C_1$–$C_5$) and 3–4% yield for coke [1–7]. To this date, most of these works were carried out in lab-scale fixed bed reactor. Rare report was found on using the fluidized bed reactor, which, however, may be much suitable for this process compared to the fixed bed, since the high temperature operation always result in the rapid deactivation of the catalyst, which called for the necessary continuous reaction and catalyst regeneration [4]. On the other hand, backmixing of gases was widely observed in the single stage fluidized bed (SSFB), which not only decreased the driving force of the conversion of gas reactants, but also increased the probability of the undesirable side reaction of intermediates over the catalyst [8–10]. Actually, over a metal–zeolite catalyst with Lewis and Brosten acids, the MTA process included many reactions such as the dehydration of methanol, hydrogen-transfer reaction from olefins to paraffins, dehydrogenation of olefins or paraffins to aromatics in presence of metal (such as Zn, Ag and Ga etc.), disproportionation, isomerization, dealkylation or alkylation of aromatics etc. [1,2,11]. It remained unknown whether the operation in fluidized bed influenced the product profiles of aromatics or not. Even worse, the product evolution in MTA process over metal–zeolite catalyst, different from those in methanol to olefins (MTO) and methanol to hydrocarbons (MTH) [11–14], was unclear yet, which increased the difficulty for the controlled production of aromatics.

In the present work, the conversion of methanol was studied not only in SSFB, but also in two stage fluidized bed (TSFB). Actually, sampling product in different stages of TSFB and the operation in TSFB varying reaction temperature provided sufficient information for the evolution of $C_1$–$C_5$ hydrocarbon and aromatics products. It allowed us to decouple this process, since most reactions above were not only acidic sensitive, but also temperature sensitive or even catalyst structure sensitive [1,11–18]. As result, we found the product evolution route of MTA is different from that of MTO and MTH [11–14]. The presence of metal over zeolite, independent of the acid amount of the catalyst, was crucial to convert liquefied petroleum gas (LPG) and $C_{5+}$ alkanes and alkenes into aromatics

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with high yield. The MTA process mainly followed a consecutive reaction route from methanol to dimethyl ether (DME), $C_1$–$C_5$ hydrocarbons and finally to aromatics. Moreover, *para*-xylene (PX) was confirmed as the primary product of aromatics, while other isomers of xylene (X) were produced by the isomerization of PX subsequently, and B, T and trimethylbenzene (TriMB) was produced by the dealkylation and alkylation of X finally. These knowledge help us to understand the different MTA products in SSFB and TSFB. High yield of aromatics in TSFB, compared to the SSFB, was due to the inhibition of backmixing of gaseous reactants and intermediates [8–10]. These results were not only useful for the further understanding of the catalytic issue on the product profiles, but also provided engineering solutions for the scale up.

## 2. Experimental

### 2.1. Catalyst preparation

The model catalyst used here was a Zn/ZSM-5 based catalyst with the loading of Zn of 3%. Zn was firstly doped on the ZSM-5 with Si/Al molar ratio of 38 by soaking the microsized ZSM-5 powder in the solution of 0.5 mol $L^{-1}$ $Zn(NO_3)_2$ at 100 °C for 24 h. Then the powder was filtrated and washed by de-ion water for 5 times, then was dried firstly at 105 °C for 48 h and calcinated at 650 °C for 6 h. The powder was grinded to an average size of 100 μm. In addition to the fresh catalyst, the catalyst was also treated in 700 °C in 100% steam for 6 h. We called it here as spent catalyst with weak acids [4] used for the comparison study.

Acidity of the catalyst was analyzed by $NH_3$–TPD in a Quantachrome automated chemisorption analyzer from room temperature to 850 °C with a ramp of 10 °C $min^{-1}$. Brunauer–Emmett–Teller (BET) surface area of catalyst are recorded in a Quantachrome automated surface area and porosity analyzer with $N_2$ as the adsorption gas.

Effect of Zn was to stabilize the acids of ZSM-5 and to increase the dehydrogenation ability of the catalyst [1,2]. The Zn loading of the fresh catalyst and spent catalyst was measured by the titration method. Firstly, catalyst was solved by using 0.5 mol $L^{-1}$ HCl at 50 °C for 30 h. Secondly, the soluble Zn was titrated by using EDTA. Indictor was Xylenol Orange disodium salt and the masking agent was ammonium fluoride, which was used to decrease the influence of $Al^{3+}$ in the solution. End point of titration was set when the color of solution changed from pink to light yellow. The Zn loading in spent catalyst is 98–99% of that in fresh catalyst, indicating the nearly unchanged Zn loading after the reaction.

### 2.2. MTA experiment in fluidized bed reactor

For MTA reaction in SSFB (Fig. 1 left), 600 g catalyst was directly added into the reactor. For the operation in TSFB, 400 g catalyst was added in the lower stage of TSFB (Fig. 1 right), which was close to the bottom distributor, 200 g catalyst was added in the upper stage of TSFB. A perforate plate with pore size of 1 mm was placed between the lower and upper stage in order to avoid the mixing of catalysts in different stages. Thus the information of gases or liquid product and the catalysts in different stages can be obtained separately. Temperature range was 250–475 °C, pressure was 0.4–0.5 MPa (absolute pressure) and gross space velocity of methanol was 0.2–0.6 g $g^{-1}$ cata $h^{-1}$.

The product flowing out of the reactor was directly sent to the GC (Shimadzu, GC2014, Japan, equipped with two flame ionization detectors (FID)). One FID was used to detect hydrogen, CO, $CO_2$ and gaseous hydrocarbons with carbon number of 1–6. Another was used to analyze the methanol, dimethyl ether (DME), hydrocarbons with carbon number of 5–14. The pipe between reactor and GC was heated to 160 °C by the hot wires outside to avoid the condensation of water, hydrocarbons with carbon number larger than 4. Yield of aromatics was calculated by the carbon base, without considering the amount of water. The analysis using GC gave a resolution of 10 ppm for the component of product.

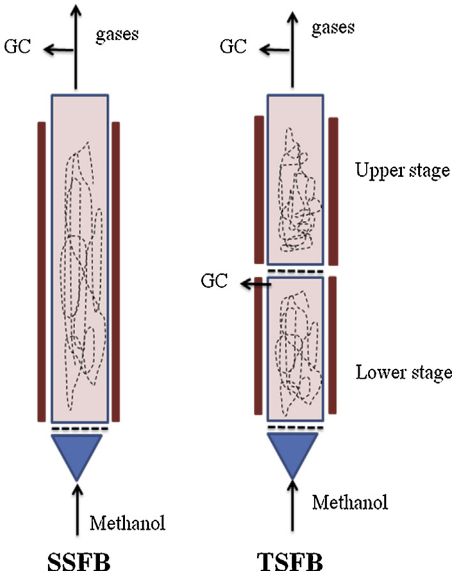

**Fig. 1.** Illustration of single stage fluidized bed (SSFB) and two stage fluidized bed (TSFB).

Since the catalyst had relatively long life time and the activity of the catalyst can be well regenerated by burning coke, the experimental data used in the present work remained very good repeatability.

## 3. Result and discussions

### 3.1. Characterization of the fresh and spent catalysts

BET surface area of fresh and spent catalyst was 136.4 and 137.3 $m^2$ $g^{-1}$, respectively, indicating its stable pore structure. The doping of Zn on HZSM-5 mainly resulted in the formation of Lewis acids in large amount, which was favorable to increase the dehydrogenation ability of the catalyst [1,2]. In addition, the modification of zeolite by Zn also stabilized the middle strong acids [1]. Fig. 2 showed the $NH_3$–TPD result of fresh and spent catalyst. The treatment by steam under high temperature resulted in the significant decrease in the amount of weak acidity in 200–350 °C and strong

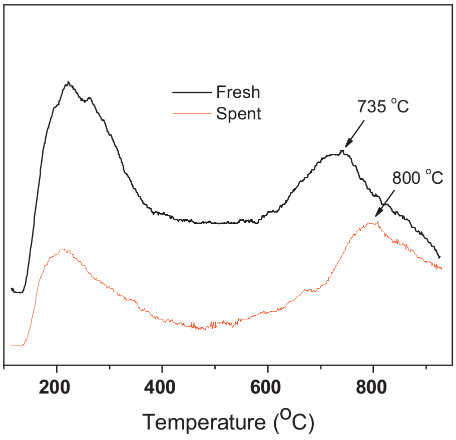

**Fig. 2.** $NH_3$–TPD of fresh and spent catalyst of Zn/ZSM-5.